NBSIR 73-254

A Mercury Vapor Generation and Dilution System

E. P. Scheide, R. Alvarez, B. Greifer, E. E. Hughes, J. K. Taylor

National Bureau of Standards
Department of Commerce
Washington, D. C. 20234

October 1973

Final Report

Prepared for
National Institute for Occupational Safety and Health
Division of Laboratories and Criteria Development
Cincinnati, Ohio 45202

NBSIR 73-254

A MERCURY VAPOR GENERATION AND DILUTION SYSTEM

E. P. Scheide, R. Alvarez, B. Greifer, E. E. Hughes, J. K. Taylor

National Bureau of Standards
Department of Commerce
Washington, D. C. 20234

October 1973

Final Report

Prepared for
National Institute for Occupational Safety and Health
Division of Laboratories and Criteria Development
Cincinnati, Ohio 45202

U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

A Mercury Vapor Generation and Dilution System

ABSTRACT

This report describes a system capable of producing well-defined test atmospheres of mercury in air or other diluent gas at concentrations between 0.005 and 0.5 µg/l and an analytical system for the analysis of these gas mixtures. Various parameters that affect the generator and analytical system and their interactions are discussed. This gas delivery system provides a means of calibration of the various analytical systems for mercury now in use. The analytical unit of the system can also be used for the determination of mercury in industrial atmospheres by collecting the mercury on a silver wool collector, and then desorbing it by heat into a flameless atomic absorption spectrometer.

1. INTRODUCTION

This report describes a system capable of producing well-defined test atmospheres containing concentrations of mercury for the calibration of analytical instruments and evaluation of analytical methodology. The system developed and described was designed to produce concentrations in the industrially important range of 0.005 to 0.5 µg/l but other concentrations could be achieved by suitable adjustment of the operational parameters.

2. EXPERIMENTAL

2.1 Apparatus

Mercury lends itself readily to the evaporation method for generating test atmospheres. Basically, this entails saturating the gas of interest with mercury and diluting the subsequent test gas to achieve the concentrations desired.

A schematic of the mercury generation system is shown in Figure 1. Two streams of air pass through silica gel/charcoal driers and filters to remove impurities. One stream goes through a differential flow controller (DFC-1), a regulating valve (V-2), and a high flow rotameter (FM-1), to the mixing chamber. This stream is subsequently used as the dilution air. The other stream flows through a differential flow controller (DFC-2), an on-off valve (V-3), a regulating valve (V-4), through a low flow rotameter (FM-2) and into the

saturation unit. The saturation unit is composed of two parts; a heater-vaporizer and a condenser. The air stream, upon passing through the heater-vaporizer unit, becomes saturated with mercury at a relatively high temperature. It then passes into a condenser unit where it cools rapidly and any excess mercury collects on the mercury pool present in the condenser. The temperature of the condenser determines the concentration of the mercury-in-air stream. This stream then passes into the mixing chamber where it is diluted with the other air stream, and then into a manifold where samples can be withdrawn. The condenser is connected to a constant-temperature water-circulating bath, containing anti-freeze effective to -5°C. The bath maintains temperatures between 0°C and 26°C to at least ±0.1°C.

2.2 Analysis

The method used for analysis of the mercury concentrations was similar to that described by Long, Scott, and Thompson [1]. Analyses were made by withdrawing samples from the manifold at 200 cc/min and collecting the mercury on silver wool. The mercury was then desorbed by a controlled heating cycle and measured using a flameless atomic absorption spectrometer. The spectrometer was calibrated by injecting a known volume of saturated mercury vapor onto the silver wool, using a "head-space" technique from standards kept at a very constant and well known temperature. A block diagram of the mercury generation and analysis system is shown in Figure 2.

3. PERFORMANCE EVALUATION

3.1 Calibration

As stated previously, the mercury generation system was calibrated by injection of known volumes of saturated air. A comparison of the atomic absorption signals given by these standards and samples taken from the generation system is shown in Figure 3. The non-linearity of the line is due to the non-linearity of the atomic absorption instrument and not to the generation system.

3.2 Sampling

When samples of mercury are absorbed onto the silver wool collector and then heated to desorb the mercury for analysis, recorder traces similar to those shown in Curve A of Figure 4 are obtained. The peak shape, though not symmetrical, is very reproducible so that the peak height can be measured and compared with standards to determine the amount of mercury in the sample.

An alternative to collecting the mercury samples on silver wool and then heating to desorb them would be to connect the atomic absorption instrument directly to a sampling port of the generation system and monitor the mercury output continuously. Curve B of Figure 4 shows the type of graph obtained. The sensitivity is not as great as in the first method, but this is not serious, since a mercury concentration of 0.005 µg/l will still give a recorder deflection. However, the analyzer must be previously calibrated for this mode of operation by some other technique.

3.3 Response Time

As indicated in Curve B of Figure 4, the response time in producing a steady-state concentration of mercury vapor upon going from one concentration to another is about 5 minutes at concentrations not too different from each other, and about 10 minutes when large concentration changes are made. The response time is about the same in going from high to low and from low to high concentrations. It is recommended that 10 minutes elapse after changing concentrations before taking samples.

3.4 Temperature Effects

Initially, upon comparing the calculated and observed mercury concentrations from the generation system, a difference of about 7 percent was noticed, with the output higher than that calculated. It was determined that the cause of this discrepancy was a temperature difference between the water bath-circulator and the condenser. To correct this problem, the condenser and the water lines were insulated and a copper - constantan thermocouple was installed at the condenser in order to accurately measure its temperature. The temperature difference using the modified arrangement is about 0.3°C at 0.0°C, which will cause results that are 3 percent higher without a temperature correction. If the temperature is measured and corrected for, the calculated and observed values are the same. When the condenser is operated at room temperature, its temperature may be considered that of the bath.

The optimum condenser temperature for the concentration range of interest was determined to be 0°C for concentrations between 0.005 and 0.200 µg/l and 26°C for concentrations between 0.100 and 0.500 µg/l.

Experiments were also conducted in order to determine the effect of the heater saturator temperature upon the generator output. The optimum temperature difference between saturator and condenser is about 25°C. At higher temperature differences, complete condensation in the condenser does not occur and the output is higher than calculated, whereas, at lower temperature differences, complete saturation is not achieved and the output is lower than calculated. The temperature difference should be controlled at 25°C ±5°C for best results.

It should be noted that a correction to the volume of mercury saturated air must be made when there is a difference between the temperature of the condenser and of room air.

3.5 Condenser Design

Figure 5 shows the final condenser design. The condenser is imbedded in styrofoam and placed in an aluminum box which is attached to the chassis. The water inlets and outlets are connected to bulkheads at the rear of the chassis to which the water bath-circulator is connected. The water lines are insulated to minimize temperature changes of the flowing stream. The mercury pool and stainless steel wool that are placed inside the condenser are to facilitate the condensation of mercury vapor.

4. CONCLUSIONS

The system described in this report is capable of producing well-defined test atmospheres of mercury vapor in air and an analytical system is described for the analysis of these test mixtures and/or the industrial atmospheres under investigation directly. Figure 6 shows the relationship between the observed and calculated values for the output of the mercury generation system. As can be seen, the output is theoretical within the accuracy of the analysis of ±2 percent.

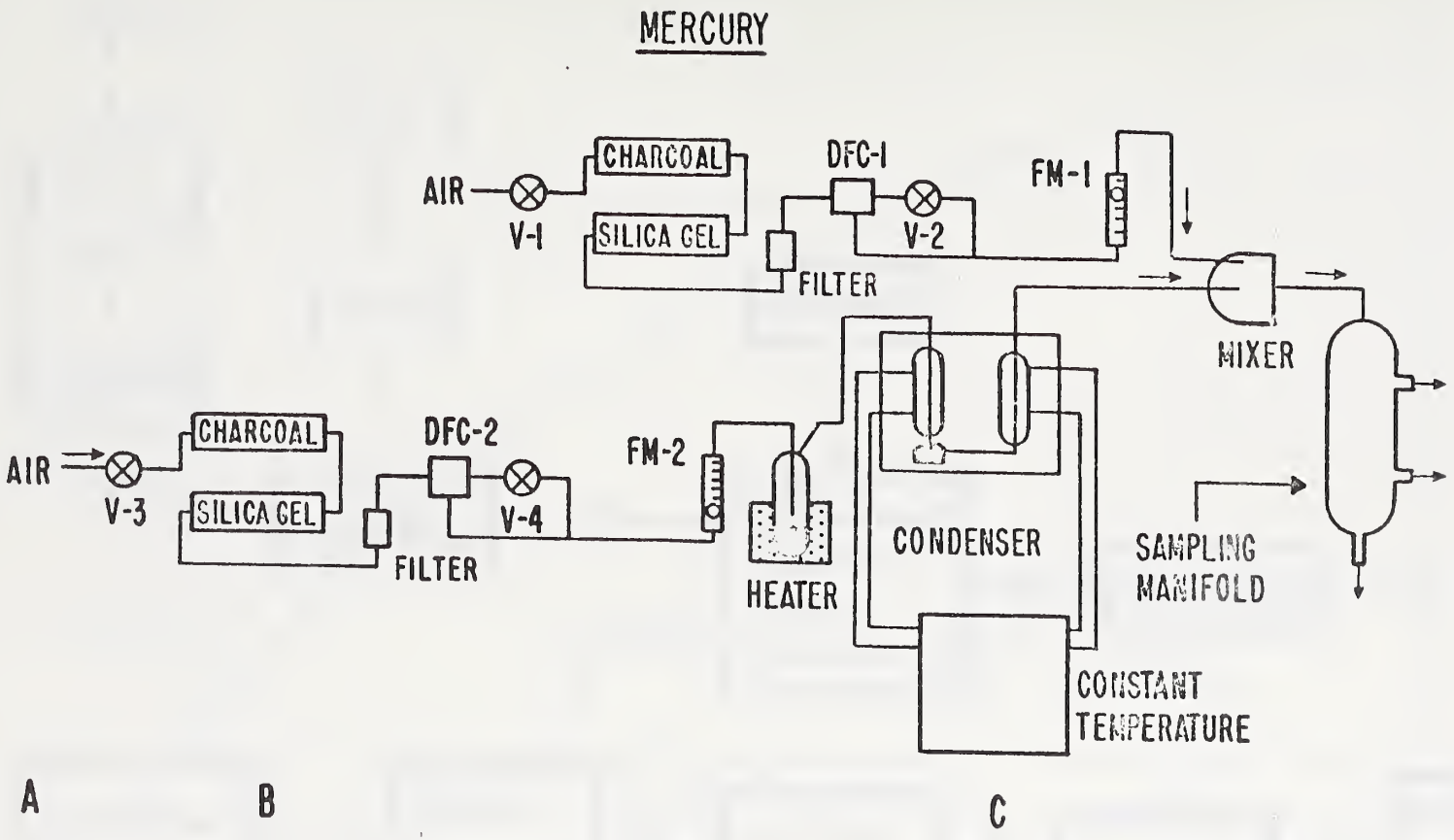

FIGURE 1. SCHEMATIC DIAGRAM OF GENERATING SYSTEM FOR MERCURY.

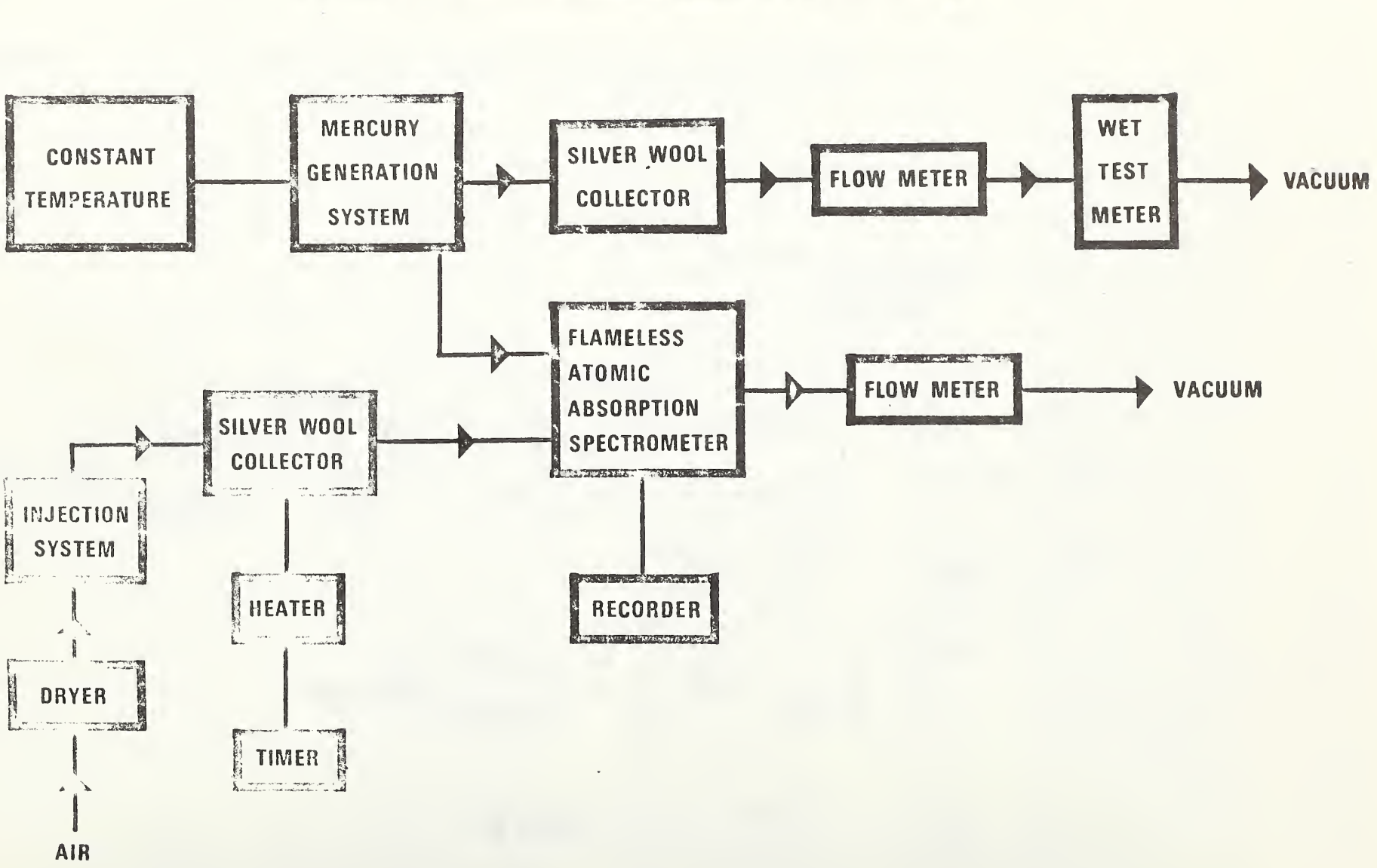

FIGURE 2. SCHEMATIC REPRESENTATION OF GENERATION AND ANALYSIS SYSTEM FOR MERCURY.

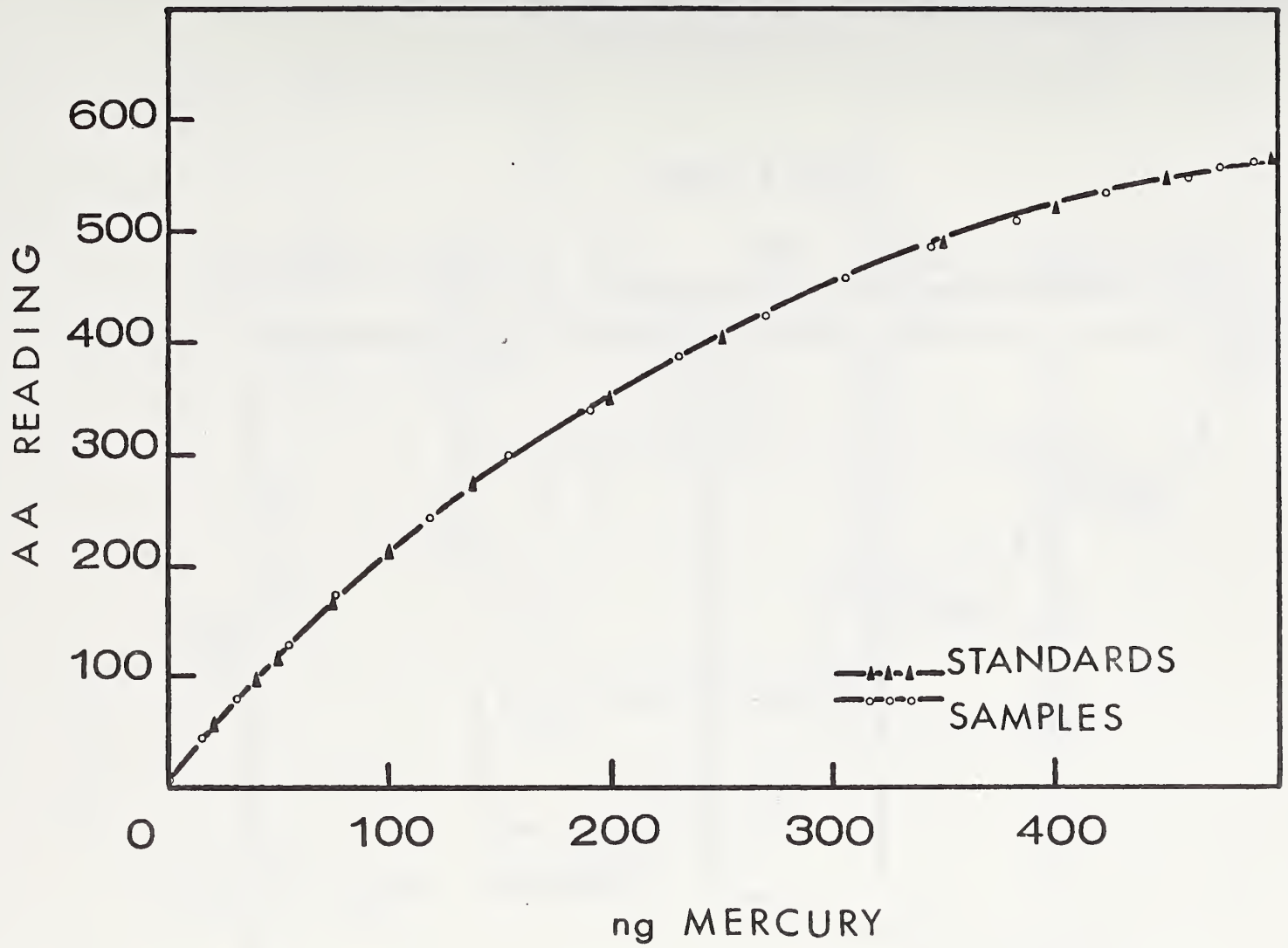

FIGURE 3. CALIBRATION OF MERCURY GENERATING SYSTEM.

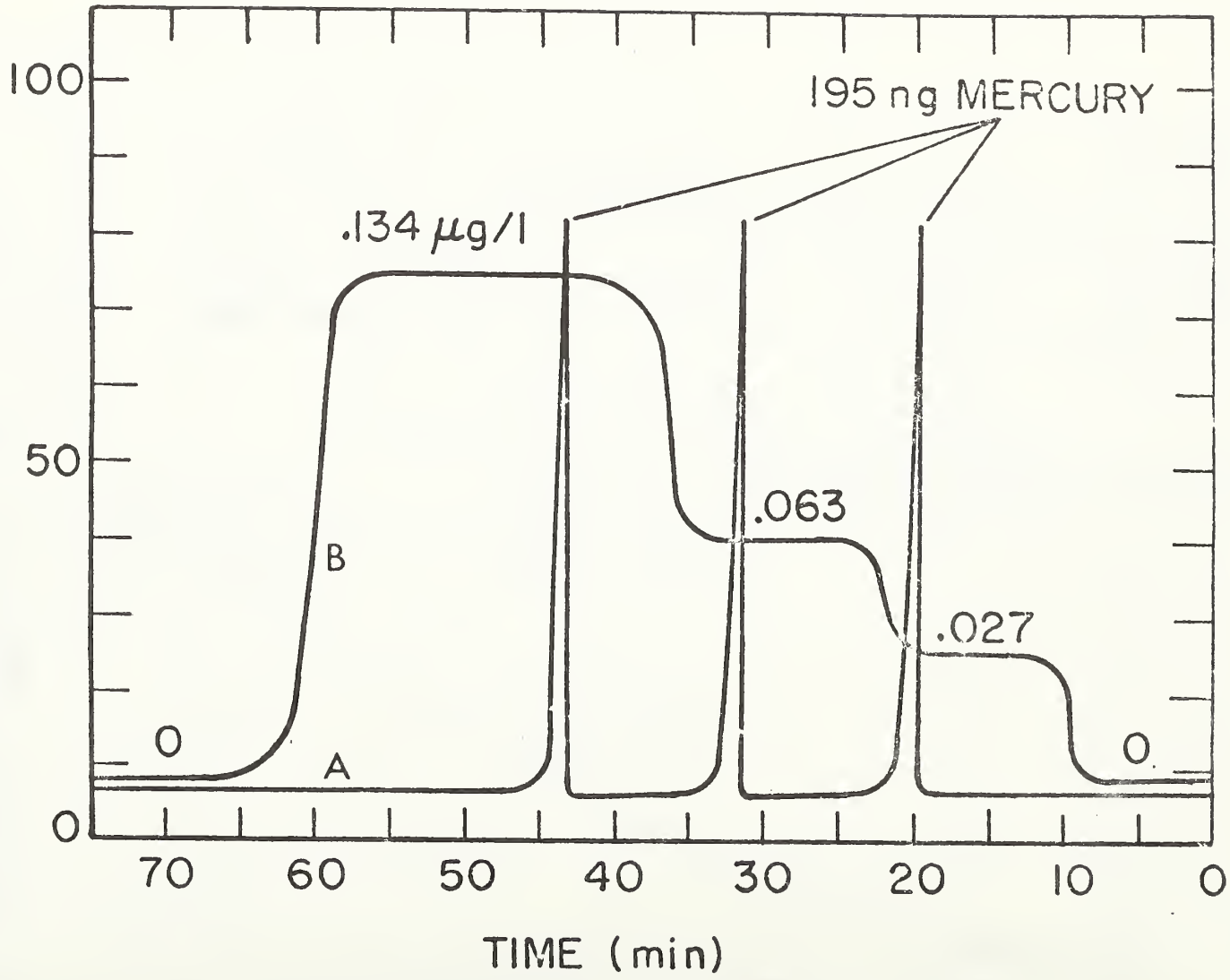

FIGURE 4. MERCURY SAMPLING AND ANALYSIS SHOWING BOTH CONTINUOUS SAMPLING AND DISCRETE SAMPLES.

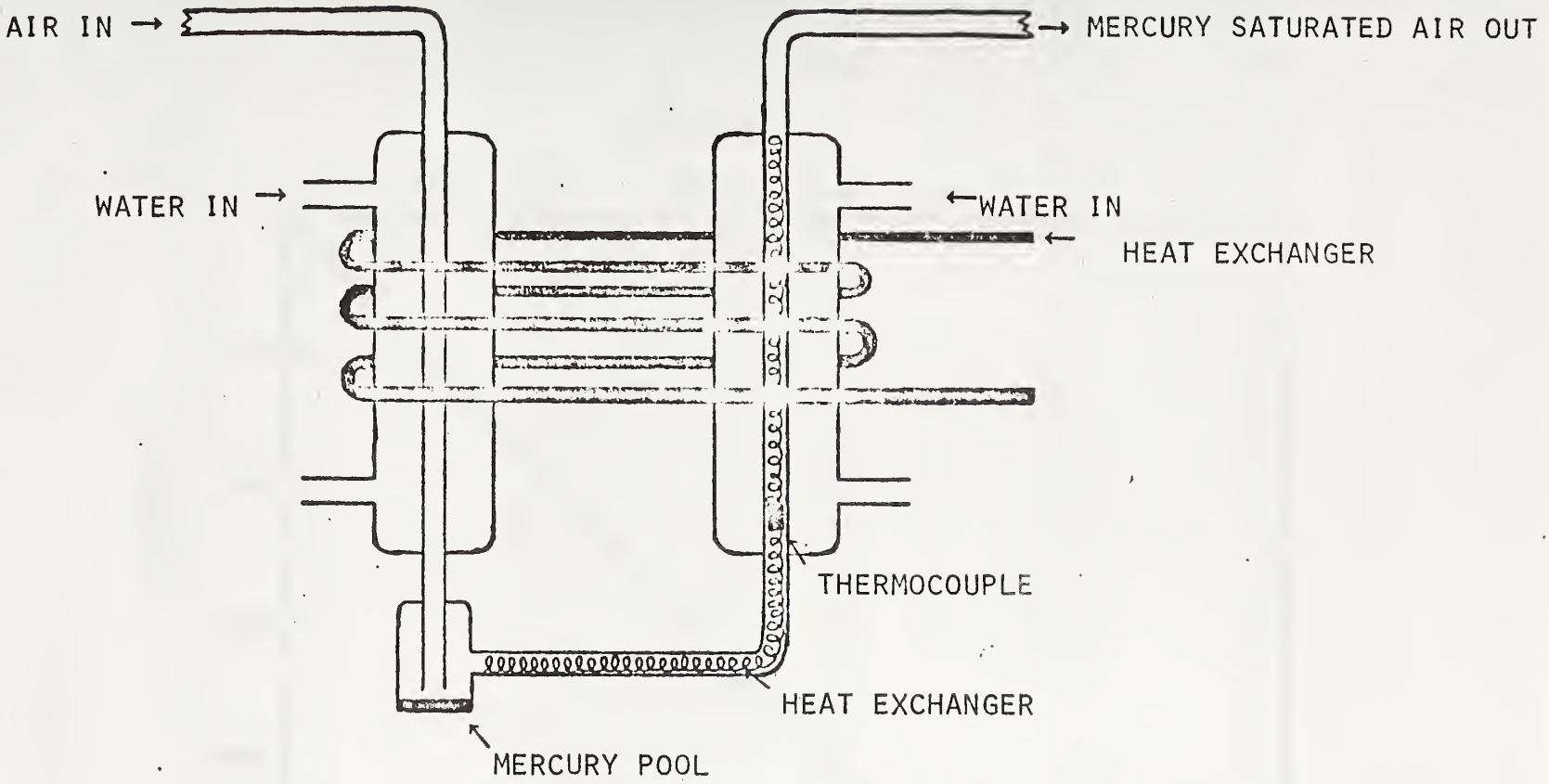

FIGURE 5. MERCURY CONDENSER.

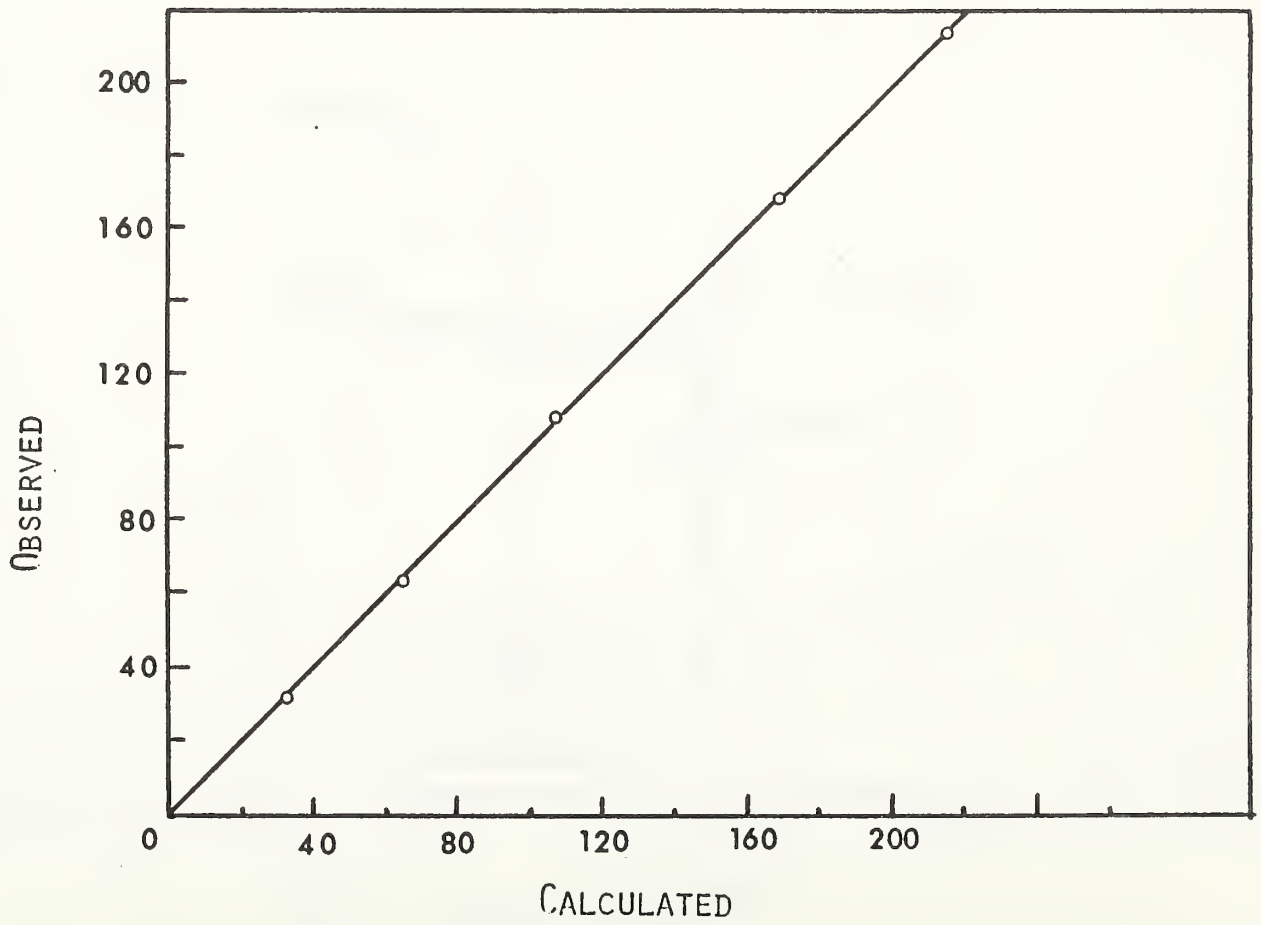

FIGURE 6. OBSERVED CONCENTRATION OF MERCURY VERSUS THE CALCULATED CONCENTRATION GENERATED WITH THE MERCURY SYSTEM.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 73-254	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

A Mercury Vapor Generation and Dilution System

5. Publication Date: October 1973

6. Performing Organization Code

7. AUTHOR(S) E.P. Scheide, R. Alvarez, B. Greifer, E.E. Hughes, and J.K. Taylor

8. Performing Organ. Report No. NBSIR 73-254

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address (*Street, City, State, ZIP*)

National Institute for Occupational Safety and Health
Cincinnati, Ohio

13. Type of Report & Period Covered: Final

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT (*A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.*)

This report describes a system capable of producing well-defined test atmospheres of mercury in air or other diluent gas at concentrations between 0.005 and 0.5~~00~~ µg/l and an analytical system for the analysis of these gas mixtures. Various parameters that affect the generation and analytical system and their interactions are discussed. This system provides a means of calibration of the various analytical systems for mercury now in use. The analytical unit of the system can also be used for the determination of mercury in industrial atmospheres by collecting the mercury on a silver wool collector, and then desorbing it by heat into a flameless atomic absorption spectrometer.

17. KEY WORDS (*six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons*) Atomic absorption; gas generation system; mercury; occupational safety.

18. AVAILABILITY

[X] Unlimited

[ ] For Official Distribution. Do Not Release to NTIS

[ ] Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13

[ ] Order From National Technical Information Service (NTIS) Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT): UNCLASSIFIED

21. NO. OF PAGES: 14

20. SECURITY CLASS (THIS PAGE): UNCLASSIFIED

22. Price


AMERICAN REVOLUTION BICENTENNIAL 1776-1976